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(54) Title: CONDUCTING ORGANIC POLYMERS (57) Abstract There is disclosed a conductimetric or piezoelectric gas sensor comprising: one or more conducting organic polymers; and gas sensitive interrogation means for interrogating a conductimetric or piezoelectric property of said one or more polymers; characterised in that at least one of the conducting organic polymers is a substituted polythiophene having a substituent moiety at the 3 position.		

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CONDUCTING ORGANIC POLYMERS

This invention relates to conducting organic polymers, methods for producing same, and gas sensors manufactured from conducting organic polymers.

Gas sensors which employ conducting organic polymers (COPs), such as polypyrrole and substituted derivatives thereof, are well known (see, for example, International Publications WO 96/00384, WO 96/00383, and K C Persaud and P Pelosi in "Sensors and Sensory Systems for an Electronic Nose", pp 237-256, eds J W Gardner and P N Bartlett, 1992, Kluwer Academic Publishers, Netherlands, and references therein). Typically, a single gas sensor is produced by depositing a layer of COP between a pair of electrodes, the sensor being operated as a chemiresistor, i.e. the presence of a gas is detected by measuring variations in the dc resistance of the COP, these variations being caused by adsorption of the gas onto the COP. It is common for a plurality of sensors to be incorporated into a single gas sensing device. The use of such arrays of COP sensors allows gases, vapours and odours to be recognised by the response "fingerprint" - the pattern of sensor responses across the array. In this manner, an impressive range of gases can be detected and identified - either individually or as components of mixtures - with good sensitivity.

However, there are a number of problems and disadvantages associated with the use of COPs in gas sensing. One problem is that COPs are usually sensitive to polar molecules, and not to non-polar molecules. One consequence of this selectivity towards polar molecules is that COP gas sensors are easily affected by changes in humidity levels because water vapour causes relatively large changes in COP conductivity. Another problem is that most COPs cannot effectively bridge electrode gaps of greater than ca. 25 μm . Larger electrode gaps than this are desirable, because larger surface areas of COP can be deposited, resulting in higher saturation thresholds. International Publication WO 96/00383 describes a method in which a bilayer of COPs is used to span

“large” electrode spacings of 100 μm and greater. The first, “base” layer of COP acts as substrate on which a second layer of a different COP is deposited. Thus, in an array of gas sensors, the individual gas sensors have the same base layer of polymer, but different second layers of COPs, which gives rise to the response “fingerprint”. However, the only COP suggested as being suitable for use as a base layer in WO 96/00383 is polypyrrole.

A disadvantage with polypyrrole, and, indeed, with most COPs in general, is that the polymers are virtually insoluble, which means that precise polymer deposition onto electrodes is quite a difficult task. It is known that various substituted derivatives of polythiophenes can be produced in conducting and non-conducting forms, and that, in the non-conducting form at least, these polymers are substantially soluble in a number of solvents such as chloroform, benzene and tetrahydronaphthalene. (See, for example, US Patent 4 737 557, European Patent Application EP 0 203 438 A1, and Canadian Patent Application CA 2070043 A1). However, the preparation of stable, conducting films of substituted polythiophenes having long chain lengths (and hence able to bridge large electrode spacings) has proved a significant problem. It is necessary that a commercial gas sensor has a working lifetime of at least three weeks, preferably much longer, and therefore it is essential that any COP utilised in a commercial gas sensor is substantially stable for at least this period of time. The use of a number of poly (3-alkylthiophenes) as gas sensitive materials is described in two papers by Ohmori *et al* (Y Ohmori, H Takahashi, T Kawai and K Yoshino, Jpn. J. Appl. Phys., 29 (1990) 1849 and Y Ohmori, K Muro and K Yoshino, Synth.Met., 55-57 (1993) 4111). In one paper, a Schottky diode was fabricated using poly (3-decylthiophene), and variations in the reverse bias current were detected when the device was exposed to a number of gases. In the reverse bias region, the polymer is in its non-conducting state. In the other paper, a Schottky gated field effect transistor (FET) was fabricated using poly (3-butylthiophene) and poly (3-ethylthiophene). Variations in the current - voltage characteristics of the devices were observed in the presence of a number of gases. In

both of these papers, the measured gas dependence is essentially due to changes in the work function of the polymer, and the devices either operate with the polymer in its non-conducting state, or with the polymer alternating between non-conducting and conducting states. Thus the mechanism of the observed gas sensitivity is different from the array based devices described above, in which gases are detected via changes in polymer conductivity. Furthermore, the papers of Ohmori *et al* do not suggest that gas sensors having certain very advantageous properties (fully described below) might be produced if poly (3-alkylthiophenes) are used in their conducting state.

The present invention overcomes the above mentioned problems, difficulties and considerations providing improved gas sensors which employ conducting, substituted polythiophenes and convenient methods for producing stable films of such conducting, substituted polythiophenes. Gas sensors of the present invention are less affected by humidity, and can employ relatively large electrode gaps. Furthermore, improved multilayers of COPs are provided by the invention.

For the avoidance of doubt, the term "gas" is understood to include all species in the gas phase, including vapours emanating from liquids or sublimed from solids.

According to a first aspect of the invention there is provided a conductimetric or piezoelectric gas sensor comprising:

one or more conducting organic polymers;

and gas sensitive interrogation means for interrogating a conductimetric or piezoelectric property of said one or more polymers;

characterised in that at least one of the conducting organic polymers is a substituted polythiophene having a substituent moiety at the 3 position.

Conductimetric sensors are sensor which rely on changes in an electrical property of the polymers, such as, dc resistance or an ac impedance quantity. FET devices which rely on changes in polymer work function, and which alternate between conducting and non-conducting states are not conductimetric gas sensors. Examples of piezoelectric gas sensors are surface acoustic wave (SAW) devices and quartz crystal devices.

The one or more conducting polymers may bridge electrodes in such a manner as to effect an electrical connection between the electrodes. The gas sensor may have a pair of electrodes. One advantage with such devices is that large electrode spacings may be bridged with polymers.

The substituted polythiophene may be substantially soluble in its non-conducting form. Devices can then be easily manufactured, due to the convenient nature of the polymer deposition.

The substituted polythiophene may comprise repeat monomer units, the monomer unit being a 3 substituted thiophene.

Alternatively, the polythiophene may comprise repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in which at least one of the constituent thiophene rings is substituted at the 3 position thereon. In this way, a regio regular polythiophene can be produced, resulting in the production of high quality film, since polymeric chains are able to pack efficiently. The oligomer unit may be a thiophene, which may be a 3,3" substituted terthiophene. The gas sensor may comprise poly (3,3"-dihexyl 2,2": 5', 2"-terthiophene).

The substituent moiety at the 3 position may be a hydrophobic group, which may be an alkyl group having greater than two carbon atoms (i.e. propyl or greater), preferably greater than five carbon atoms. The presence of hydrophobic alkyl substituents leads to excellent water vapour rejection capabilities and enhanced sensitivity towards non-polar molecules.

The gas sensitive interrogation means may comprise signal applying means for applying electrical signal across the electrodes and detection means for detecting a chosen electrical property of the polymer or polymers in the presence of a gas.

The gas sensor may comprise two or more layers of conducting organic polymer, the first layer being a substituted polythiophene having a substituent moiety at the 3 position.

The substituted polythiophene may have PF_6^- or FeCl_4^- dopant anions associated therewith.

According to a second aspect of the invention there is provided the use of a conducting organic polymer for sensing gases, characterised in that the conducting organic polymer is a substituted polythiophene having a substituent moiety at the 3 position.

Examples of uses are in conductimetric and piezoelectric gas sensors, but such as FET sensors, not sensors which rely, at least in part, on the polymer being present in its non-conducting state.

The polythiophene may be substantially soluble in its non-conducting form.

The substituent moiety may be a hydrophobic group, may be an alkyl group having greater than two carbon atoms, preferably greater than five carbon atoms.

The substituted polythiophene may have PF_6^- or FeCl_4^- dopant anions associated therewith.

According to a third aspect of the invention there is provided the use of a substituted polythiophene for sensing gases, characterised in that the polythiophene comprises repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in which at least one of the constituent thiophene rings is substituted at the 3 position thereon.

Examples of uses include use in conductimetric, piezoelectric and FET type gas sensors - on other words, the gas sensing is not constrained to the use of the polymer in its conducting form.

The oligomer unit may be a terthiophene which may be a 3,3" substituted terthiophene. Poly (3,3"-dihexyl-2,2": 5', 2"-terthiophene).

According to a fourth aspect of the present invention there is provided a multilayer comprising at least two layers of conducting organic polymer, in which the first layer of conducting organic polymer comprises a substituted polythiophene having a substituent moiety at the 3 position and the second layer of conducting organic polymer is deposited onto the first layer.

The polythiophene may be substantially soluble in its non-conducting form.

The substituted polythiophene may comprise repeat monomer units, the repeat monomer unit being a 3 substituted thiophene.

Alternatively, the polythiophene may comprise repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in which at least one of the constituent thiophene rings is substituted at the 3 position thereon. The oligomer unit may be an terthiophene, which may be a 3,3" substituted terthiophene. The multilayer may comprise poly (3,3"-dihexyl-2,2":5'2"-terthiophene).

The substituent moiety may be a hydrophobic group, which may be an alkyl group having greater than two carbon atoms, preferably greater than five carbon atoms.

The substituted polythiophene may have PF_6^- or FeCl_4^- dopant anions associated therewith.

The multilayer may be a component of a gas sensor.

According to a fifth aspect of the invention, there is provided a conducting substituted polythiophene having a substituent moiety at the 3 position and having PF_6^- or FeCl_4^- dopant anions associated therewith. Such polymers produce stable films.

According to a sixth aspect of the invention there is provided a method for manufacturing a gas sensor according to the first aspect of the invention comprising the steps of:

providing a solution of the substituted polythiophene polymer, in its non-conducting form, dissolved in a solvent;

applying said solution to a substrate;

removing the solvent to produce a deposit of the substituted polythiophene polymer in its non-conducting form; and

doping the deposit of substituted polythiophene polymer to produce the conducting form of said polymer.

The solution may be spin coated onto the substrate.

The doping of the deposit of polymer may be performed electrochemically or chemically.

Deposited polythiophene polymer may be removed from selected areas of the gas sensor.

Embodiments of methods, polymers and devices in accordance with the invention will now be described with reference to the accompanying drawings, in which:-

Figure 1 shows a generalised COP based gas sensor;

Figure 2 shows (a) head to tail and (b) head to head polymer conformations;

Figure 3 shows a generalised formula of a poly-3,3" substituted terthiophene; and

Figure 4 shows a reaction scheme for the production of poly (3,3"-dihexyl-2,2":5',2" - terthiophene);

A major aspect of the present invention is the provision of a conductimetric gas sensor (shown schematically in Figure 1) comprising:

a pair of electrodes 10, 12;

one or more conducting organic polymers (COPs) 14 bridging the pair of electrodes in such manner as to effect an electrical connection between the pair of electrodes 10, 12;

and gas sensitive COP interrogation means 16, 18;

characterised in that at least one of the COPs is a substituted polythiophene having a substituent moiety at the 3 position.

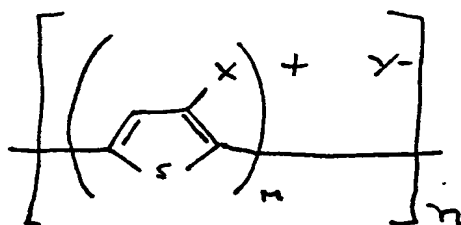
The gas sensitive interrogation means 16, 18 comprises signal applying means 16 for applying an electrical signal across the electrodes and detection means 18 for detecting a chosen electrical property of the COP or COPs in the presence of a gas. Typically, a dc electrical signal is applied to the electrodes by the signal applying means 16 and the dc resistance of the COP or COPs 14 is measured. This procedure is well known in the art (see, for example, Persaud & Pelosi, *ibid*, and references therein). However, it should be noted that other COP interrogation methodologies are possible, such as the application of ac electrical signal followed by the detection of certain ac properties (see GB 2 203 553 and WO 97/19349).

Furthermore, it is possible to provide piezoelectric gas sensors, such as SAW and quartz devices, which comprise COP(s) of the type described above. The operation and fabrication of piezoelectric devices is well known to those skilled in the art. Gas selection is accomplished by measuring shifts in resonant frequency inclined by changes in the mass of the device caused by adsorption of gases onto the device. In the

context of the present invention it is the COP which provides a surface for adsorption of gases thereon.

An important class of substituted polythiophene COP comprises repeat monomer units, the repeat unit being a 3 substituted thiophene.

In the conducting form, the generalised formula describing such substituted polythiophenes is :



where X is the substituent moiety at the 3 position on the thiophene repeat units, n is a natural number, and Y⁻ is a dopant anion. m is a number, greater than one, which represents the number of thiophene units per unit positive charge on the polymer.

An important advantage with gas sensors employing these polymers is that that the polymers can successfully bridge large electrode spacings of 100 μm or greater. Another important advantage is that the polymers may be substantially soluble in their undoped, non-conducting form, a property which permits a range of convenient gas sensor fabrication techniques to be employed. Another important advantage still is that, when the substituent moiety at the 3 position is a hydrophobic group, gas sensors may be produced which exhibit excellent water vapour rejection characteristics and enhanced responses to non-polar molecules. The hydrophobic group can be an alkyl group having greater than two carbon atoms (e.g. propyl), preferably greater than five carbon atoms (e.g. hexyl). Branched alkyl substituents (i.e., secondary and tertiary alkyl(s)) might be used. These alkyl substituted polythiophenes have the advantage that they are substantially soluble. However, it will be apparent that other substituent groups which

have hydrophobic properties might also be employed, such as benzyl or tolyl based substituent groups. Partially fluorinated or per fluorinated alkyl substituents might be used. Substituent groups need not be of entirely hydrocarbon character : indeed, polar linkages might be used, provided that the tail of the substituent group is hydrophobic. In this way, the outer "sheath" of the polymer is hydrophobic, and water vapour is not permitted to adsorb onto the polymer.

It is possible that the water vapour rejection capability of these substituted polythiophenes derives from the combination of the hydrophobic nature of the substituent groups and the inherent configuration of the polymeric "backbone". Alkyl substituted polythiophenes adopt tightly packed conformations in the non-conducting state due to a marked propensity for "head to tail" linkages of the type shown in Figure 2a. Other COPs may adopt more open structures, allowing small molecules such as water to penetrate into the polymer backbone, negating the effect of hydrophobic substituents. This explanation is in keeping with the observation that substituted polypyrroles having large alkyl substituents (dodecyl and greater) do not exhibit marked water vapour rejection capabilities. However, it should be emphasised that this is a tentative suggestion which has yet to be confirmed.

Another important class of substituted polythiophene COP comprises repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in which at least one of the constituent rings is substituted at the 3 position thereon. An important, but non-limiting example, is a poly-3,3" substituted terthiophene, shown in generalised form in Figure 3 where n is a natural number. For convenience of presentation the charge balance is not shown in Figure 3.

An advantage of the structure shown in Figure 3 compared to polythiophenes composed of 3-substituted thiophene monomers is that, in the former, one in three thiophene units do not possess a substituent moiety. This provides more "molecular space", so that dopant ions are able to access the polymer backbone and interact more

strongly with this backbone, resulting in greater polymer stability. A reduction in steric hinderance might also be a factor.

A further advantage is that a regia regular polythiophene can be produced in which there are no head to head linkages. This enables the production of high quality polycrystalline films, since the individual polymer chains can pack very efficiently. Additionally, the conjugation length of the polymer is increased, resulting in a smaller band gap material with higher electronic mobility. The regioregular nature of the polymer stems from the specific stereochemistry of the oligomer, which in turn is a consequence of the reaction scheme employed (see below).

A further advantage still is that many poly (3,3" substituted terthiophene are soluble.

Other substituted oligomers are within the scope of the invention. It might be possible to use a 3' substituted terthiophene, or to use oligomers having different numbers of constituent thiophene rings, such as substituted bithiophenes or oligomers having four thiophene rings. Indeed, variation of factors such as the number of thiophene rings in the oligomer, the number of and positions of the substituent groups, and the nature of the substituent groups can be accomplished in order to facilitate access of dopant ions to the polymer backbone. Whilst, desirably excluding water molecules. The amount of "molecular space" available for such an important parameter as is the hydrophobicity of the substituents. Preferred substituents are alkyl groups, such as hexyl. The comments made above in respect of hydrophobic substituents apply here: in particular, fluorinated and/or branched alkyl substituents can be employed.

Soluble substituted polythiophenes, such as the 3-alkyl polythiophenes and 3,3" alkyl poly (terthiophenes) described above, are particularly useful because gas sensors may be conveniently manufactured by a method comprising the steps of :-

providing a solution of the substituted polythiophene polymer, in its non-conducting form, dissolved in a solvent;

applying the solution to a substrate;

removing the solvent to produce a deposit of the substituted polythiophene polymer in its non-conducting form; and

doping the deposit of substituted polythiophene polymer to produce the conducting form of the polymer.

Preferably, the solution is spin coated onto the substrate. The spin coating process is convenient, and allows high quality sensors having uniform films of polymer to be produced. Such sensors exhibit highly reproducible response characteristics, because the polymer films are deposited in reproducible fashion.

The doping of the deposit of polymer may be performed electrochemically, or chemically, i.e. using a chemical oxidant.

Suitable substrates and electrode materials are well known in the art. Usually, the electrodes are formed on the substrate and the polymer deposited thereon. However, it is, in principle, possible to deposit the polymer onto the substrate and then to deposit the electrodes onto the polymer. Removal of solvent might be via evaporation at room, or higher, temperature.

After a non-selective deposition process such as spin coating, the deposited polythiophene polymer is removed from selected areas of the gas sensor. Photolithographic techniques may be employed, in which masks are deposited to expose

the areas of the sensor from which polymer is to be removed. The polymer may then be removed by wet or dry etching, followed by removal of the masks.

It will be appreciated that gas sensors can be fabricated using non-soluble polythiophenes. Conventional manufacturing techniques, such as electrochemical or chemical deposition, may be employed. It will also be appreciated that the general approach outlined here can be employed to produce conductimetric sensors or piezoelectric sensors. In the latter instance, the substrate is typically quartz. In the former instance, the substrate might be, for example, quartz, silicon, alumina or ceramic.

Another major aspect of the present invention is the provision of multilayers of COPs, comprising at least two layers of COP, in which the first layer of COP comprises a substituted polythiophene having a substituent moiety at the 3 position, and the second layer of COP is deposited onto the first layer. A primary use of such multilayers is as a component of a gas sensing device, although the multilayers present invention may find application in other areas in which COPs are employed, such as in the provision of conducting coatings or as components of other electrical devices. In the case of gas sensing devices, it is desirable that the device is relatively insensitive to ambient humidity levels, and therefore it is desirable that the substituent moiety is a hydrophobic group, such as an alkyl group having greater than two carbon atoms, preferably greater than five carbon atoms.

In the context of gas sensors, the use of such polythiophenes as a "base" layer in a COP multilayer is especially advantageous for the following reasons:

- 1) the polythiophenes form a good conducting substrate;
- 2) the polythiophenes provide an excellent substrate onto which a further layer of COP may be deposited;

- 3) water vapour rejection is excellent;
- 4) mechanical properties are excellent;
- 5) deposition of the soluble polythiophenes is very convenient;
- 6) large electrode gaps may be bridged.

although it will be apparent that many, or all, of these advantages apply to multilayers used in the other applications described above.

International Publication WO 96/00383 describes a method in which a bilayer of COPs is produced. However, the only material suggested as being suitable as a base layer is polypyrrole. The substituted polythiophenes of the present invention are superior to polypyrrole in terms of their suitability to act as base layers, due to (at least) the properties 3, 4 and 5 described above.

The preparation of stable conducting films of substituted polythiophenes has long been a problem. It has been found that the use of PF_6^- or FeCl_4^- dopant anions produces films of enhanced stability. PF_6^- is especially preferred as the dopant anion.

Example 1 : Preparation of Poly (3-hexylthiophene)

In a 250 ml three-necked flask FeCl_3 (3.95 g, 0.02 mol) was dissolved in 100 ml CHCl_3 (previously dried over an activated molecular sieve). This solution was allowed to stir at room temperature under a nitrogen atmosphere. To this solution was added 3-hexylthiophene (Aldrich Chemical Company Limited, Gillingham, UK) (1.00 g, 0.0059 mol) in 20 ml CHCl_3 dropwise over a period of 10 minutes. The contents of the vessel were then allowed to stir for 18 hours. Over this course the reaction mixture

turned from a yellow-brown to blue-black colour, the latter being characteristic of the conducting form of the polymer. The volume of the reaction mixture was then reduced by removing the chloroform on a rotary evaporator to leave a black solid. This solid was then placed inside an extraction thimble and purified by soxhlet extraction with methanol. A red polymer was produced. This was dried at 50°C under reduced pressure using a BUCHI-TO-51 vacuum oven. The red colouration is characteristic of the undoped, non-conducting form of the polymer. The yield was 91%.

¹H nmr data (CDCl₃, TMS):

δ 7.0 (s, 1H thiophene), δ 2.8 (m, 2H, CH₃-thiophene (80%)), δ 2.5 (m, CH₂-thiophene (20%)). δ 1.2 (m, 11H, CH₂ and CH₃).

The methylene nmr data indicate that some 80% of the polymer is present in a head to tail configuration, whilst the remaining 20% adopts a head to head (or tail to tail) configuration.

Example 2 : Gas Sensors Using Poly (3-hexylthiophene)

Film formation : the red polymer of Example 1 was substantially soluble (ca. 60%) in chloroform and toluene. A chloroform solution of the polymer was prepared by dissolving the polymer and filtering off excess insoluble material. This produced a red-orange solution which was then concentrated by allowing the chloroform to evaporate slowly. The resulting solution was then dripped onto a 32 way sensor array of a type used commercially by the assignees (AromaScan, Crewe, UK). The array had previously been cleaned in iso-propanol. The separation of adjacent electrodes in the array is 250 μm. The red polymer film was seen to coat the array as the solvent evaporated. Films of high quality were produced.

The polymer films were then chemically doped by immersing in a 1M FeCl_3 solution (in 1-methoxy-2-propanol) for 30 minutes. The film turned blue-black upon insertion of the FeCl_4^- dopant ion. Purification was carried out by an acetone wash followed by a chloroform wash. The film was allowed to dry. The average resistance of gas sensors in the array was 3000 Ω , and the resistance values remained substantially constant over a period of three weeks.

Response to solvent vapours : the sensor was placed in a commercially available analyser unit and its response to a variety of vapours was monitored, using techniques well known in the art. Laboratory air was employed as a reference gas, and a water wash was performed between each sample.

The response of a gas sensor is given by $\frac{\Delta R}{R} \times 100\%$ - the percentage change measured in the basal dc resistance R when the gas sensor is exposed to a vapour. The basal resistance is the value measured when the sensor is exposed to the reference gas.

The following average $\frac{\Delta R}{R} \times 100\%$ responses were observed:

Toluene	(40-50%)
Ethyl Acetate	(15-25%)
Hexane	(40%)
Water	(0.50%)
Butanol (62 ppm)	(0%)

These measurements were repeated on further arrays with similar results.

The responses to vapours containing the polar OH group are negligible, whilst the responses to non-polar vapours are extremely large, showing massive enhancements in sensitivity relative to gas sensors employing "standard" COPs.

Example 3 : Preparation of Gas Sensors Having A COP Bilayer

A computer controlled EG&G PARC 263A potentiostat connected to a Keithley 7001 multiplexer was used for all electrochemical experiments. Standard 32-way ceramic substrates were used for polymer deposition and Pt mesh (Aldrich) was used as a counter/reference electrode. Tetraethylammonium hexafluorophosphate (TEAPF₆) (Aldrich) was recrystallised from hot ethanol and dried in a BUCHI vacuum oven for two hours. Acetonitrile (hplc grade, Aldrich) was used as received. All monomer solutions were prepared from 100% acetonitrile 0.1 M TEAPF₆ solutions. These were all thoroughly degassed by bubbling N₂ through them for one hour. Poly (3-hexylthiophene) base layers were deposited by preparation of a 0.01 g/ ml CH₃Cl solution and evaporation of 1ml of this solution over the electrode areas of the array. This provided a fairly thick layer of red polymer.

From cyclic voltammetry experiments it was found that application of 1.90 V to the undoped poly (3-hexylthiophene) film produced a sufficiently doped film with no over-oxidation. This potential was therefore consistently used in all experiments.

The chemically formed film was placed into a degassed 0.1 M PF₆ solution and the potential of 1.90 V applied for 30 seconds. The film was dipped once into acetonitrile to remove residual electrolyte salt and then given a 5 minute chloroform wash. During this second wash it was clear that there was still undoped material within the film as this was seen to dissolve into solution.

The resistances of films in the thirty two sensors were measured, and were found to be spread across the range 750 Ω to 20 K Ω . The array was then placed into a degassed acetonitrile 0.1M TEAPF₆, 0.1M N-dodecylpyrrole solution and a potential of 1.90 V was applied to all thirty two sensors for 15 seconds. The sensors were then washed in acetonitrile and chloroform, this process being repeated. The resistances of

the sensors were measured, and were found to be rather higher than the resistances of the single layer of poly (3-hexylthiophene).

The array was exposed to a number of solvent vapours using the method described in

Example 2. The following ($\frac{\Delta R}{R} \times 100\%$) responses were observed:

Ethyl acetate	(8-12%)
Toluene	(20-40%)
Hexane	(25-35%)
Water	(-0.5 - -1.0%)
Ethanol	(-2 - -6%)

The presence of the second layer of COP appears to tighten up the range of responses, but the overall characteristics - rejection of highly polar molecules, in particular water vapour, and enhanced sensitivity towards non-polar molecules - remains.

The responses were remeasured after 48 hours and similar results were obtained, indicating that the system is reasonably stable. Furthermore, after five days, basal resistances had increased by ca. 20%, which represents an acceptable degree of stability.

Example 4 : Spin Coating with Poly C3-hexylthiophene

An improved deposition scheme involves spin-coating the polymer onto a substrate. Using the 32 way sensor array described above, it was found that a 2ml chloroform solution of between 0.20 and 0.40g of poly (3-hexylthiophene) is sufficient to produce sensor films of acceptance thickness. Best results are produced using 0.25g of polymer in 2ml chloroform, the solutions being spun at 1000 rpm for 30 seconds.

Example 5: Preparation of Poly (3,3''-dihexyl-2,2'': 5', 2''-terthiophene) (PDHTT)

The reaction scheme is shown in Figure 4.

2-iodo-3-hexylthiophene

A solution of 3-hexylthiophene (5 g, 29.8 mmol) in benzene was stirred at 0°C. Mercuric oxide (6.4 g, 29.8 mmol) and iodine (7.5 g, 29.8 mmol) were then added alternately in small aliquots over a period of one hour. The mixture was stirred for 10 hours at room temperature and then filtered. The filtrate was concentrated and the residue distilled under vacuum to yield 2-iodo-3-hexylthiophene as a colourless oil (108-110°C/mm) 5.6 g, 63%.

3,3''-dihexyl-2,2':,2''-terthiophene

To a flask equipped with a reflux condenser, a solution of 2-iodo-3-hexylthiophene (5.6 g, 18.9 mmol) in diethyl ether (20 mL) was added dropwise at 0°C under nitrogen to magnesium turnings (0.69 g, 28.3 mmol) in ether (20 mL). After the reaction had subsided the mixture was stirred for a further 2 hours at room temperature. The Grignard reagent thus formed was added via canula to a stirred solution at 0°C of 2,5-diiodothiophene (Aldrich) (2.9 g, 8.6 mmol) and 1,3-bis(diphenylphosphino)propane)-nickel(II)chloride (0.34 g, 0.63 mmol) in diethyl ether (20 mL) under nitrogen. A vigorous reaction ensued and the mixture was stirred for a further 1 hour at room temperature before being poured into water. The organic layer was washed with water (2 x 50 mL), dried (MgSO₄) and concentrated. The residue was purified by chromatography (silica gel: hexane) to afford the desired product in 36% yield.

Poly(3,3''-dihexyl-2,2':,2''-terthiophene) (PDHTT)

To a stirred suspension of anhydrous FeCl_3 (0.9 g, 5.56 mmol) in anhydrous chloroform (20 mL) under a nitrogen atmosphere at room temperature was added all at once a solution of 3,3''-dihexyl-2,2':5',2''-terthiophene (0.58 g, 1.39 mmol) in chloroform (20 mL). After three hours the reaction was quenched with methanol (20 mL) and filtered. The black solids thus obtained were extracted with methanol followed by acetone in a Soxhlet apparatus. The remaining solids were suspended in chloroform (50 mL) and stirred with an aqueous solution of hydrazine until all the solids were suspended in chloroform (50 mL) and stirred with an aqueous solution of hydrazine until all the solids had dissolved in the organic phase to produce a bright orange solution which was separated, washed with water (3x 50 mL) and concentrated. The deep red solids obtained were dried under vacuum to yield 310 mg, 18% of poly(3,3''-dihexyl-2,2':5',2''-terthiophene).

^1H nmr 300 MHz (CDCl_3): 1.92 (s, 60H), 1.25-1.50 (m, 120H), 1.67 (m, 40H), 2.78 (t, 40H), 6.95 (d, 1H), 7.03 (s, 19H), 7.10 (s, 19H), 7.19 (d, 1H).

Example 6, Gas Sensors Using PDHTT

The red PDHTT polymer of Example 5 was used to fabricate gas sensors substantially using the method described in Examples 2 and 3

A film of PDHTT was deposited on a 32 way sensor array comprising a ceramic substrate (AromaScan plc) by evaporation of a chloroform solution (20 mg/mL). The film was then patterned by a photolithographic process to provide 32 individual sensor elements. This base layer of the array was doped with PF_6^- as counterion (0.9V vs Ag/AgCl, 0.1M tetraethylammonium hexafluorophosphate in acetonitrile). The following monomers were polymerised as top layers to produce multilayers: two

dithienyl pyrroles, bithiophene, an N-alkanoyl substituted pyrrole and an N-alkyl substituted pyrroles).

General characteristics of the array

Top Layer Material (Monomer)	Factor Increase in Resistance Per Month
base layer only	1.3
N-alkyl substituted pyrroles	3.3
dithienyl pyrroles	1.6
N-alkanoyl pyrrole	2.6
bithiophene	2.0

Table 1. Electrical stability of the sensor array under atmospheric conditions.

Top Layer Material (Monomer)	Percentage Change In Resistance Upon Exposure To Gas			
	<u>water</u> ^a	<u>ethyl acetate</u> ^b	<u>toluene</u> ^b	<u>ethanol</u> ^c
base layer only	1.1	64	17	10
N-alkyl substituted pyrroles	2.3	47	12	19
dithienyl pyrroles	1.9	48	16	17
N-alkanoyl pyrrole	3.2	54	8	27
bithiophene	2.8	47	6	24

- a) representing a change in relative humidity from 43% to 68%
- b) saturated vapour, background relative humidity 43%
- c) containing 5% water

Table 2. Response of the sensor array to water vapour and some organic solvent vapours.

Property	PDHTT	Polypyrrole
Percentage increase in resistance per month	1.3	1.5
% dR/R on exposure to water vapour (change in relative humidity from 43% to 68%)	1.1	30.

Table 3. Comparison of the PDHTT base layer with polypyrrole base layer.

The responses to water of a PDHTT sensor and a polypyrrole sensor were investigated, and the results are shown in Table 3. The Table also shows variations in basal resistances.

The data indicates that the response of PDHTT based sensors to organic vapours is substantially less affected by background humidity than similar polypyrrole based sensors.

CLAIMS

1. A conductimetric or piezoelectric gas sensor comprising:

one or more conducting organic polymers;

and gas sensitive interrogation means for interrogating a conductimetric or piezoelectric property of said one or more polymers;

characterised in that at least one of the conducting organic polymers is a substituted polythiophene having a substituent moiety at the 3 position.
2. A conductimetric gas sensor according to claim 1 in which the one or more conducting polymers bridge electrodes in such as to effect an electrical connection between the electrodes.
3. A conductimetric gas sensor according to claim 2 having a pair of electrodes.
4. A gas sensor according to any of claim 1 to 3 in which the substituted polythiophene is substantially soluble in its non-conducting form.
5. A gas sensors according to any of claims 1 to 4 in which the substituted polythiophene comprises repeat monomer units, the repeat monomer unit being a 3 substituted thiophene.
6. A gas sensor according to any of claims 1 to 4 in which the polythiophene comprises repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in

which at least one of the constituent thiophene rings is substituted at the 3 position thereon.

7. A gas sensor according to claim 6 in which the oligomer unit comprises a thiophene.
8. A gas sensor according to claim 7 in which the oligomer unit comprises a 3,3" substituted terthiophene.
9. A gas sensor according to claim 8 comprising poly (3,3"-dihexyl-2,2":5',2"-terthiophene).
10. A gas sensor according to any previous claims in which the substituent moiety at the 3 position is a hydrophobic group.
11. A gas sensor according to claim 10 in which the hydrophobic group is an alkyl group having greater than two carbon atoms, preferably greater than five carbon atoms.
12. A gas sensor according to any of claims 2 to 11 in which the gas sensitive interrogation means comprise signal applying means for applying an electrical signal across the electrodes and detection means for detecting a chosen electrical property of the polymer or polymers in the presence of a gas.
13. A gas sensor according to any of claims 1 to 12 comprising two or more layers of conducting organic polymer, the first layer being a substituted polythiophene having a substituent moiety at the 3 position.

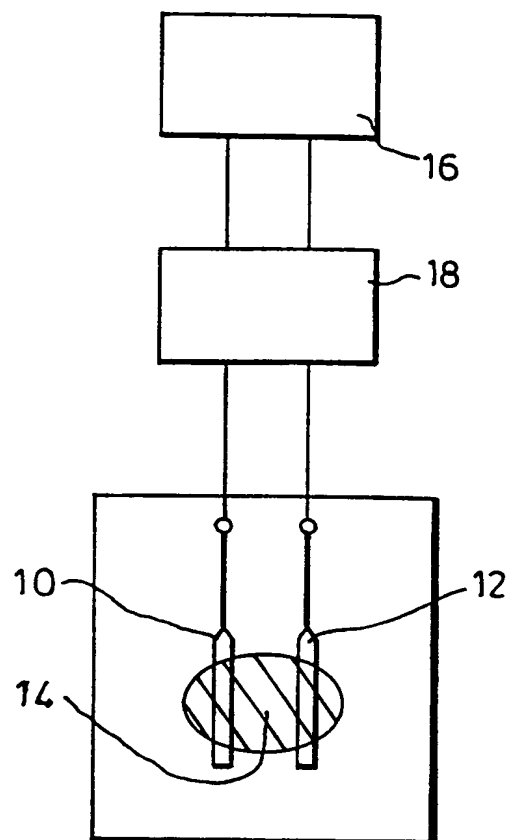
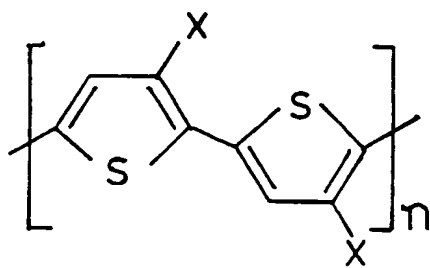
14. A gas sensor according to any of claims 1 to 13 in which the substituted polythiophene has PF_6^- or FeCl_4^- dopant anions associated therewith.
15. The use of a conducting organic polymer for sensing gases, characterised in that the conducting organic polymer is a substituted polythiophene having a substituent moiety at the 3 position.
16. Use according to claim 15 in which the substituted polythiophene is substantially soluble in its non-conducting form.
17. Use according to claim 15 or claim 16 in which the substituent moiety is a hydrophobic group.
18. Use according to claim 17 in which the substituent moiety is an alkyl group having greater than two carbon atoms, preferably greater than five carbon atoms.
19. Use according to any of claims 15 to 18 in which the substituted polythiophene has PF_6^- or FeCl_4^- dopant anions associated therewith.
20. Use of a substituted polythiophene for sensing gases, characterised in that the polythiophene comprises repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in which at least one of the constituent thiophene rings is substituted at the 3 position.
21. Use according to claim 20 in which the oligomer unit is a terthiophene.
22. Use according to claim 21 in which the oligomer unit comprises a 3,3" substituted terthiophene.

23. The use of poly (3,3"-dihexyl-2,2":5', 2"-terthiophene) for sensing gases.
24. A multilayer comprising at least two layers of conducting organic polymer, in which the first layer of conducting organic polymer comprises a substituted polythiophene having a substituent moiety at the 3 position, and the second layer of conducting organic polymer is deposited onto the first layer.
25. A multilayer according to claim 24 in which the substituted polythiophene is substantially soluble in its non-conducting form.
26. A multilayer according to claim 24 or claim 25 in which the substituted polythiophene comprises repeat monomer units, the repeat monomer unit being a 3 substituted thiophene.
27. A multilayer according to claims 24 or claim 25 in which the polythiophene comprises repeat oligomer units, the repeat oligomer unit being a thiophene oligomer in which at least one of the constituent thiophene rings is substituted at the 3 position.
28. A multilayer according to claims 27 in which the oligomer unit is a terthiophene.
29. A multilayer according to claim 28 in which the oligomer unit comprises a 3.3" substituted terthiophene.
30. A multilayer according to claim 29 comprising poly(3,3"-dihexyl-2,2":5',2"-terthiophene).
31. A multilayer according to any of claims 24 to 30 in which substituent moiety is a hydrophobic group...

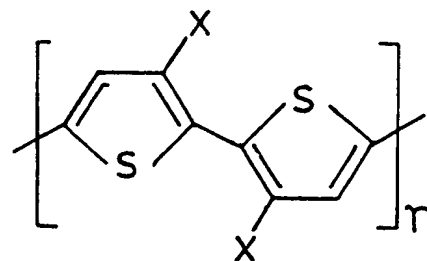
32. A multilayer according to claim 31 in which the hydrophobic group is an alkyl group having greater than two carbon atoms, preferably greater than five carbon atoms.
33. A multilayer according to any of claims 24 to 32 in which the substituted polythiophene has PF_6^- or FeCl_4^- dopant anions associated therewith.
34. A multilayer according to any of claims 24 to 33 as a component of a gas sensor.
35. A conducting substituted polythiophene having a substituent moiety at the 3 position and having PF_6^- or FeCl_4^- dopant anions associated therewith.
36. A method for manufacturing a gas sensor according to any of claims 1 to 14 comprising the steps of:
- providing a solution of the substituted polythiophene polymer, in its non-conducting form, dissolved in a solvent;
 - applying said solution to a substrate;
 - removing the solvent to produce a deposit of the substituted polythiophene polymer in its non-conducting form; and
 - doping the deposit of substituted polythiophene polymer to produce the conducting form of said polymer.
37. A method according to claim 36 in which the solution is spin coated onto the substrate.

38. A method according to claim 36 or claim 37 in which the doping of the deposit of polymer is performed electrochemically.
39. A method according to any of claims 36 to 38 in which the doping of the deposit of polymer is performed chemically.
40. A method according to any of claims 36 to 39 in which deposited polythiophene polymer is removed from selected areas of the gas sensor.

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FIG.1

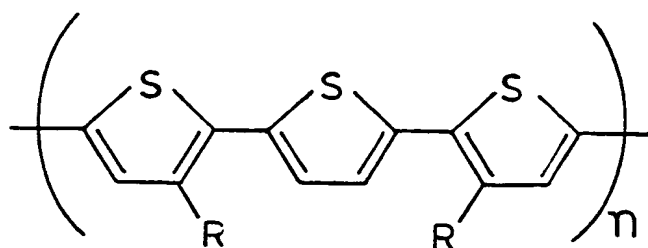
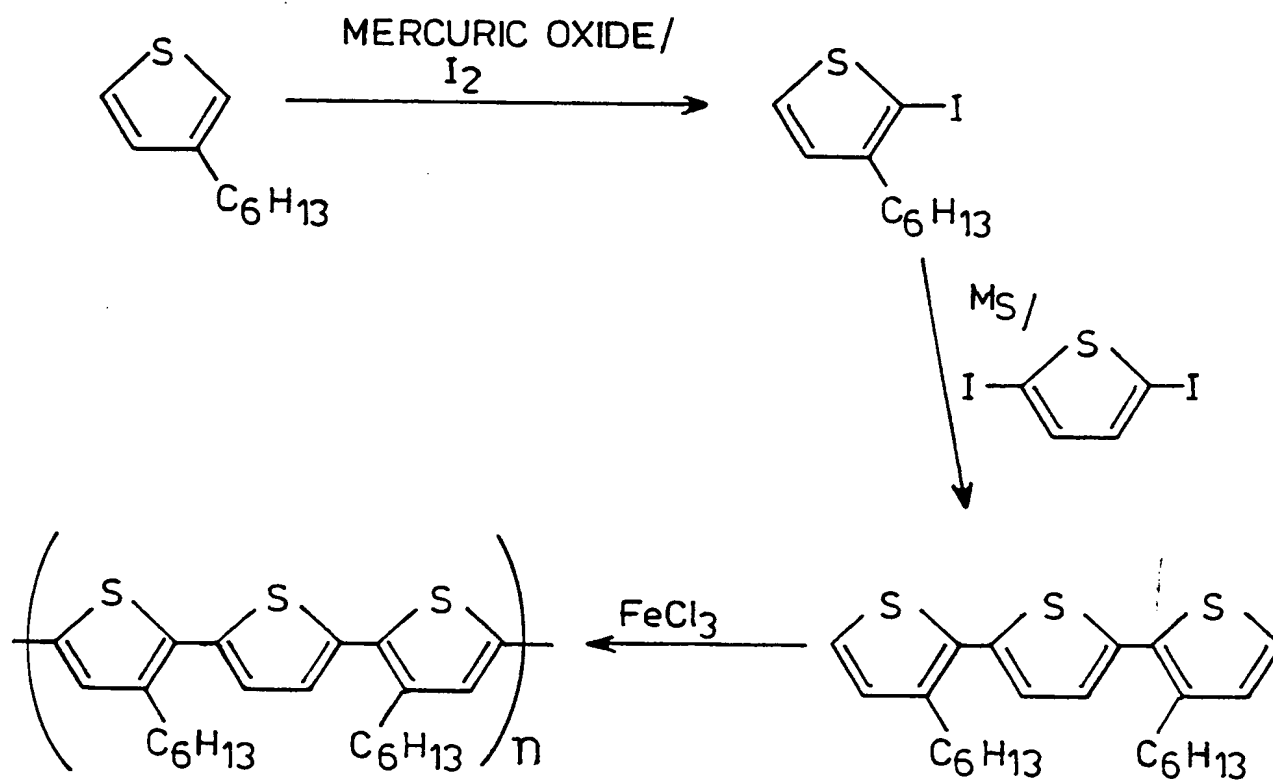
2(a)



2(b)

FIG.2

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FIG. 3FIG. 4

INTERNATIONAL SEARCH REPORT

National Application No.

PCT/GB 98/03778

A. CLASSIFICATION OF SUBJECT MATTER

G 01 N 27/12, H 01 B 1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G 01 N, H 01 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OHMORI, Y. et al. Gas-sensitive and temperature-dependent schottky gated field effect transistors utilizing poly(3-Alkylthiophene)s. Synthetic Metals, 1993, Vol. 57, pages 4111-4116 (cited in the application).	1-3, 12, 15
Y	--	4, 10, 11, 14, 19, 35
Y	US 4737557 A (SATO et al.) 12 April 1988 (12.04.88), (cited in the application).	4
Y	WO 87/00677 A1	10, 11,

☒ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

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Date of the actual completion of the international search

08 April 1999

Date of mailing of the international search report

29.04.99

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03778

-2-

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	(NESTE OY) 29 January 1987 (29.01.87) . -----	14, 19, 35

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/GB 98/03778 SAE 218277

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
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This Annex lists the patent family
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cited in the above-mentioned inter-
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4737557	12-04-88	JP A2 62220518 JP B4 1011209	28-09-87 23-02-89
WO A1 8700677	29-01-87	DE C0 3689770 DE T2 3689770 EP A1 231309 EP B1 231309 FI A0 852888 FI A 852888 FI B 74715 FI C 74715 JP T2 63500461	11-05-94 04-08-94 12-08-87 06-04-94 24-07-85 25-01-87 30-11-87 10-03-88 18-02-88